



Dithiobiurets: a novel class of acid corrosion inhibitors for mild steel

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Abstract

The corrosion inhibition behaviour of some substituted dithiobiurets, namely, -1,5-diphenyl-2,4-dithiobiuret (DPDTB), 1-tolyl-5-phenyl-2,4-dithiobiuret (TPDTB), 1-anisidyl-5-phenyl-2,4-dithiobiuret (APDTB), 1-chlorophenyl-5-diphenyl-2,4-dithiobiuret (CPDTB) were studied in 1 to 5 M HCl on mild steel. The characteristics of these compounds are explained in terms of factors such as inhibitor concentration, acid concentration, temperature, immersion time and molecular structure. Potentiodynamic polarization and a.c. impedance techniques were used to investigate the inhibition mechanism. Among the compounds studied APDTB exhibited the best performance giving more than 98% inhibition efficiency (IE) in HCl solutions. DPDTB and CPDTB were found to reduce hydrogen permeation through mild steel in HCl solutions. The adsorption of APDTB was also confirmed by Auger electron spectroscopy (AES).

1. Introduction

The inhibitive power of organic corrosion inhibitors has been interpreted in terms of many different characteristics such as molecular size, molecular weight, molecular structure and nature of the heteroatoms present in molecule [1]. Organic compounds containing both nitrogen and sulphur atoms are of particular interest as they give better IE than those containing N or S alone [2, 3]. Among these thiourea and its derivatives have been investigated extensively [4–8]. Schmitt [9] has reported that thiourea derivatives are highly toxic and induce permeation of hydrogen into the metal causing hydrogen embrittlement; therefore, the use of these compounds is not safe.

In continuation of our work on development of acid corrosion inhibitors [10–12], we have synthesized four substituted dithiobiurets, namely, 1,5-diphenyl-2,4-dithiobiuret (DPDTB), 1-tolyl-5-phenyl-2,4-dithiobiuret (TPDTB), 1-anisidyl-5-phenyl-2,4-dithiobiuret (APDTB), 1-chlorophenyl-5-phenyl-2,4-dithiobiuret (CPDTB) to investigate their inhibiting action on the corrosion of mild steel in 1 to 5 M HCl.

The selection of inhibitors is based on the following considerations: (i) they possess a lone pair of electrons on two sulphur and three nitrogen atoms in addition to π electrons of the phenyl rings through which they can adsorb readily on the metal surface, and (ii) their toxicity is very low.

2. Experimental details

Mild steel strips having chemical compositions 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P, the remainder being Fe, were used. Weight loss measurements were carried out using steel strips of size 2 cm \times 2 cm \times 0.25 cm whereas the potentiodynamic polarization, electrochemical impedance and hydrogen permeation studies were carried out with steel strips having an exposed area of 1 cm². The specimens were polished mechanically with emery papers of 1/0 to 4/0 grade and degreased with trichloroethylene.

Dithiobiurets were synthesized as described elsewhere [13, 14] and were characterized by i.r. hydrochloric acid of AR grade and triple distilled water were used for preparing test solutions of 1, 3 and 5 M HCl.

2.1. Corrosion weight loss studies

The weight loss measurements were carried out as described elsewhere [15]. Mild steel strips were immersed in 160 ml of inhibited and uninhibited solutions according to ASTM standards [16] for 3 h at 40 °C in 1–5 M HCl. 500 ppm of each inhibitor was tested in 1 M HCl at 40, 50, 60 and 70 °C for 1 h. The 500 ppm of each inhibitor was tested in 1 M HCl for 96 h at room temperature. The inhibition efficiency and corrosion rates in the presence of the inhibitors were calculated by weight loss.

2.2. Potentiodynamic polarization studies

Electrochemical potentiodynamic polarization studies were carried out using an EG&G PARC potentiostat/galvanostat (model 175), and an X-Y recorder (model RE 0089). The cell assembly consisted of mild steel as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All experiments were performed at $35 \pm 2^\circ\text{C}$.

2.3. Electrochemical a.c. impedance studies

Nyquist plots in 1 M HCl solution and inhibited solutions were obtained over the frequency range 100 mHz to 10 kHz at open circuit potential using an electrochemical impedance analyser (EG&G PARC system model M 6310) with software (M 398) according to known procedure described elsewhere [17].

2.4. Hydrogen permeation studies

Hydrogen permeation studies were carried out at a temperature of $30 \pm 2^\circ\text{C}$ using an adaption of Devanathan and Stachurski's modified two-compartment cell [18, 19]. Hydrogen permeation currents were recorded using an X-Y-t Rikadenki recorder in the presence and absence of inhibitor in 1 M HCl.

2.5. Auger electron spectroscopic studies

Auger electron spectroscopic studies were carried out on inhibited and uninhibited mild steel samples using Auger electron spectroscopy: (Varian CMA VT-112). Specimens were polished using different grades of emery paper and then dipped in inhibited acid solution containing 500 ppm APDTB for 3 h, rinsed with triple distilled water and dried at room temperature. Specimens were fixed on a fast-entry air lock (Feal) chamber maintained at a vacuum level of 10^{-11} torr. After degassing the specimens were transferred to the prepa-

ration chamber. Specimens were kept long enough to facilitate further degassing. The specimen was then introduced into the analyser chamber. The area of interest was selected with the help of a scanning electron microscope (SEM) attached to the instrument and excited with a 3 keV electron beam.

3. Results and discussion

3.1. Weight loss studies

The molecular structures of the compounds under study are shown in Table 1. Various corrosion parameters such as percentage inhibition efficiency (IE) and corrosion rate (CR) obtained by the weight loss method at different inhibitor concentrations in the 1 to 5 M HCl range are given in Table 2. It is evident that all the compounds inhibit corrosion of mild steel at all concentrations under study. The percentage inhibition efficiency for all the inhibitors increases with increase in inhibitor concentration (Figure 1(A)). All the compounds show maximum inhibition efficiency at 500, 700 and 1000 ppm in 1, 3 and 5 M HCl, respectively. The percentage inhibition efficiency for different dithiobiurets decreases in the following order: APDTB > TPDTB > DPDTB > CPDTB.

The superior performance of APDTB as corrosion inhibitor compared to TPDTB can be attributed to the presence of the effective electron releasing group $-\text{OCH}_3$, leading to greater adsorption of methoxy substituted dithiobiuret (APDTB) on the mild steel surface than the methyl substituted derivative (TPDTB). Quraishi et al. have also explained the higher IE of methoxy benothiazole as compared to methyl substituted benzothiazole on the basis of the inductive effect [20].

The lesser value of IE for CPDTB as compared to DPDTB may be attributed to the $-I$ effect (electron withdrawing inductive effect) of the chloro group, which decreases the electron availability on the reaction site

Table 1. Name and molecular structures of the inhibitors

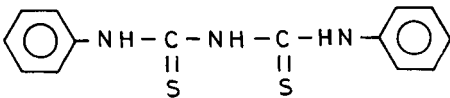
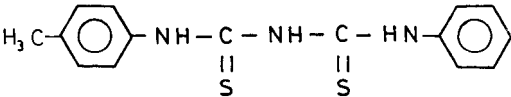
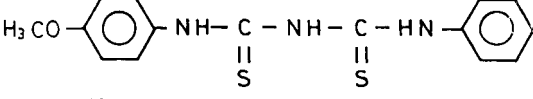
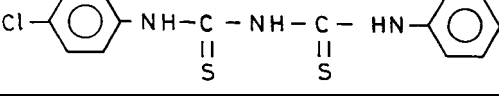
S. No.	Designation	Structural formula	Abbreviation
1	1,5-diphenyl-2,4-dithiobiuret		DPDTB
2	1-tolyl-5-phenyl-2,4-dithiobiuret		TPDTB
3	1-anisidyl-5-phenyl-2,4-dithiobiuret		APDTB
4	1-chlorophenyl-5-phenyl-2,4-dithiobiuret		CPDTB

Table 2. Corrosion parameters for different concentrations of dithiobiurets derivatives obtained from weight loss studies in 1, 3 and 5 M HCl at 40 °C for 3 h.

Inhibitor concentration /ppm	IE/%			
	APDTB	TPDTB	DPDTB	CPDTB
1 M HCl	—	—	—	—
25	96.1	93.4	92.3	88.7
50	96.4	93.9	93.4	91.2
100	97.5	95.6	94.8	91.4
200	98.1	96.9	96.1	93.7
300	98.3	97.8	97.2	94.5
400	98.6	98.1	97.6	95.6
500	98.9	98.6	98.1	95.9
3 M HCl	—	—	—	—
100	93.6	93.4	91.7	93.1
200	95.4	94.7	92.5	94.6
300	96.5	96.4	95.1	95.1
400	97.6	97.4	97.1	95.8
500	98.5	98.1	97.5	96.3
600	98.9	98.4	98.3	96.5
700	99.2	98.9	98.9	96.8
5 M HCl	—	—	—	—
200	87.5	77.1	69.4	63.4
300	91.3	83.2	77.3	71.7
500	95.1	91.2	87.9	82.6
700	98.1	95.7	92.9	92.1
1000	99.8	99.6	98.8	98.3

and causes less adsorption of chloro derivative CPDTB on the metal surface as compared to DPDTB.

The inhibition efficiency of all the substituted dithiobiurets is found to decrease with the increase in acid concentration from 1 to 5 M HCl Figure 1(B). This is due to the desorption of inhibitor molecules in strong acids.

The effect of temperature on the inhibition efficiency in 1 M HCl is shown in Figure 1(C). It was found that IE increases with increasing temperature from 40–70 °C. The increase in inhibition efficiency may be attributed to the chemisorption of dithiobiurets on the mild steel surface. The effect of immersion time on inhibition efficiency is shown in Figure 1(D). It is clear that inhibition efficiency of dithiobiurets increases with immersion time due to the formation of a barrier film which prevents acid attack on the metal surface.

3.1.1. Mechanism of corrosion inhibition

The inhibition of corrosion of mild steel in acidic solutions by DPDTB and its derivatives can be explained on the basis of adsorption on the metal surface:

- (i) Dithiobiurets exist in acid solutions as neutral molecules or in the form of cations. They can adsorb on the metal surface in the form of neutral

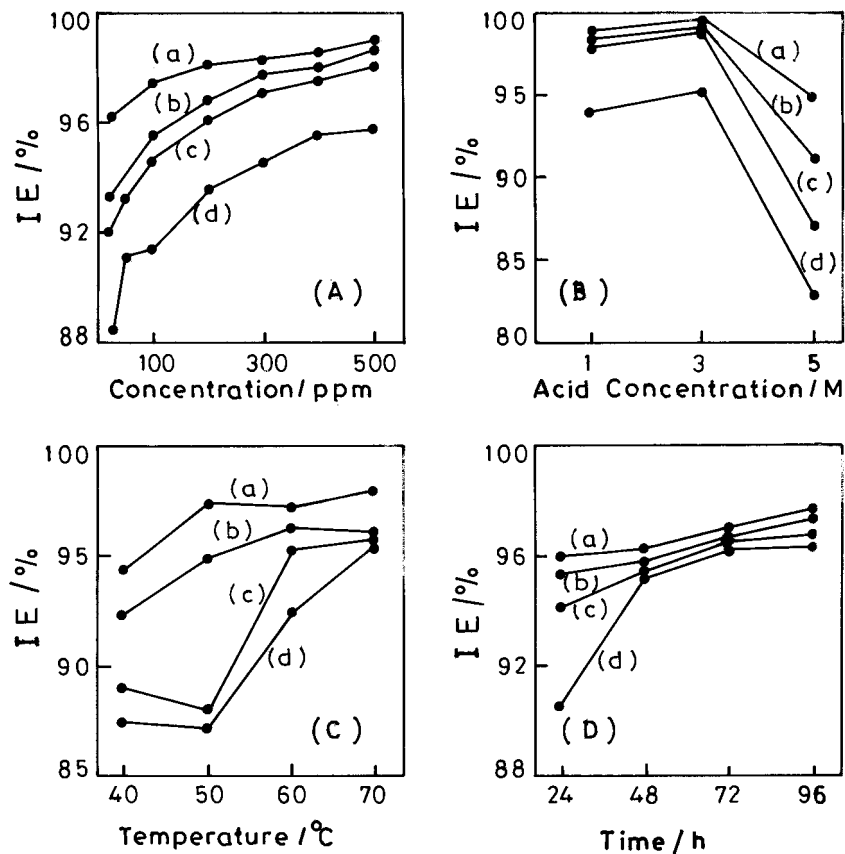


Fig. 1. Variation of inhibition efficiency: (A) with inhibitor concentration (ppm) at 40 °C in 1 M HCl; (B) with concentration (M) of HCl containing 500 ppm of inhibitor at 40 °C; (C) with temperature (°C) in 1 M HCl containing 500 ppm of inhibitor; and (D) with immersion time (h) at r.t. 25 ± 5 °C in 1 M HCl containing 500 ppm concentration of inhibitor. Curves: (a) APDTB, (b) TPDTB, (c) DPDTB and (d) CPDTB.

molecules via the chemisorption mechanism [21] involving the sharing of electrons between the atoms of nitrogen and sulphur with iron.

- (ii) Adsorption of these compounds occurs through π electron interactions between the benzene ring of the molecules and the metal surface and
- (iii) they can also adsorb on the metal surface in the form of a positively charged protonated species which can interact electrostatically with negatively charged metal surfaces [22].

The adsorption of all substituted dithiobiurets in 1 to 5 M HCl was confirmed by plotting the θ (surface coverage) against $\log C$ (concentration). The straight line obtained in all cases shows that the compounds follow a Temkin adsorption isotherm (Figure 2(A–C)).

3.2. Potentiodynamic polarization studies

Both the anodic and cathodic polarization behaviour of mild steel in 1 to 5 M HCl in the absence and presence of substituted dithiobiurets are shown in Figure 3. The I_{corr} values decrease considerably in the presence of different concentrations of inhibitor. The maximum decrease in I_{corr} value is obtained at 500, 700 and 1000 ppm in 1, 3 and 5 M HCl, respectively. The electrochemical polarization curves of TPDTB and CPDTB show the predominantly cathodic nature of the inhibition in all acidic solutions. The values of cathodic Tafel slope, b_c , for TPDTB and CPDTB are found to change with inhibitor concentration, which clearly indicates the influence of the compounds on the kinetics of the hydrogen evolution reaction. However, the value of the anodic Tafel slope, b_a , is practically constant as these compounds do not influence anodic dissolution. In the case of APDTB and DPDTB the Tafel slope values b_a and b_c remain almost constant, indicating that they are mixed type inhibitors.

3.3. Electrochemical impedance studies

Various impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}), corrosion current density (I_{corr}) and inhibition efficiency (IE) are given in Table 3. The charge transfer resistance value (R_t) is calculated from the difference in impedance at lower and higher frequencies as suggested by Haruyama and Tusru [23]. C_{dl} (double layer capacitance) values were determined using the following relation:

$$C_{\text{dl}} = \frac{1}{2\pi f(-z_{\text{immax}})R_t} \quad (1)$$

It is seen from Figures 4(A–D) that the presence of dithiobiurets increases R_t and decreases C_{dl} and I_{corr} .

3.4. Hydrogen permeation studies

Hydrogen permeation for mild steel in 1 M HCl containing 500 ppm of CPDTB and DPDTB is shown in

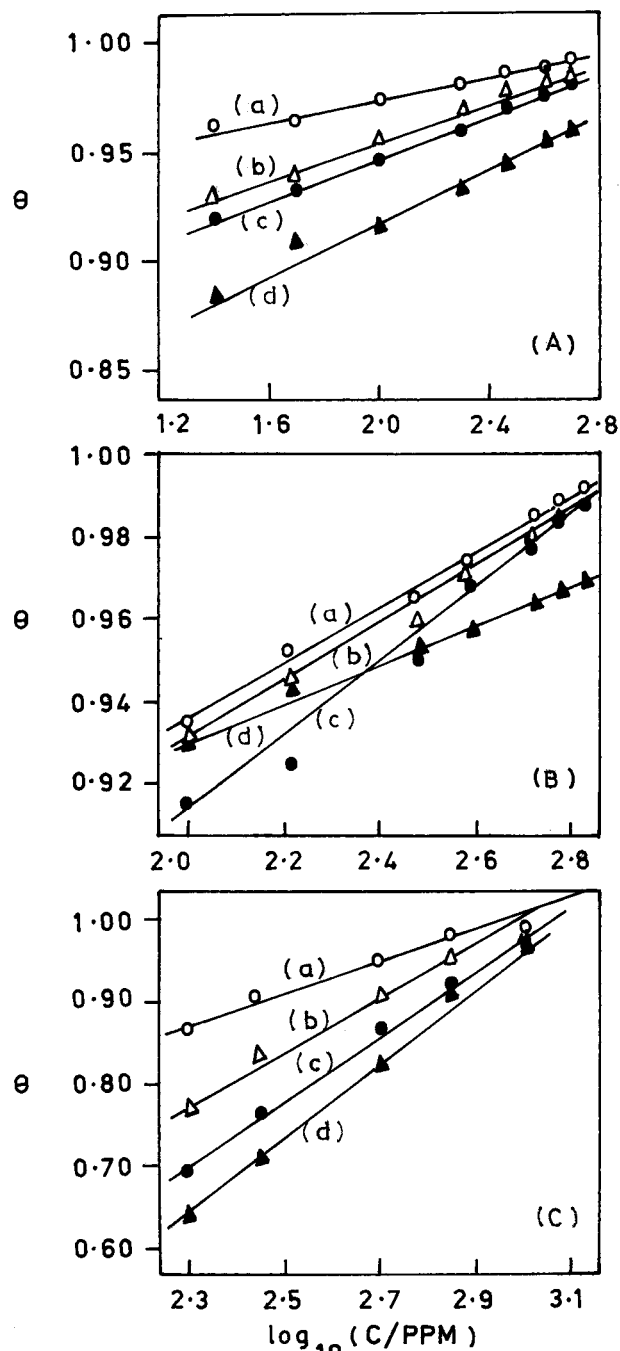


Fig. 2. Temkin adsorption isotherm plots for mild steel in (a) 1 M, (b) 3 M, (c) 5 M HCl containing dithiobiurets. Curves: (a) APDTB, (b) TPDTB, (c) DPDTB and (d) CPDTB.

Figure 5. The results show that both compounds reduce the permeation current. The reduction in hydrogen permeation current may be attributed to adsorption on the mild steel surface which prevents the permeation of hydrogen into the metal.

3.5. Auger electron spectroscopy

Auger electron spectrum obtained for plain mild steel and mild steel exposed to 1 M HCl containing 500 ppm

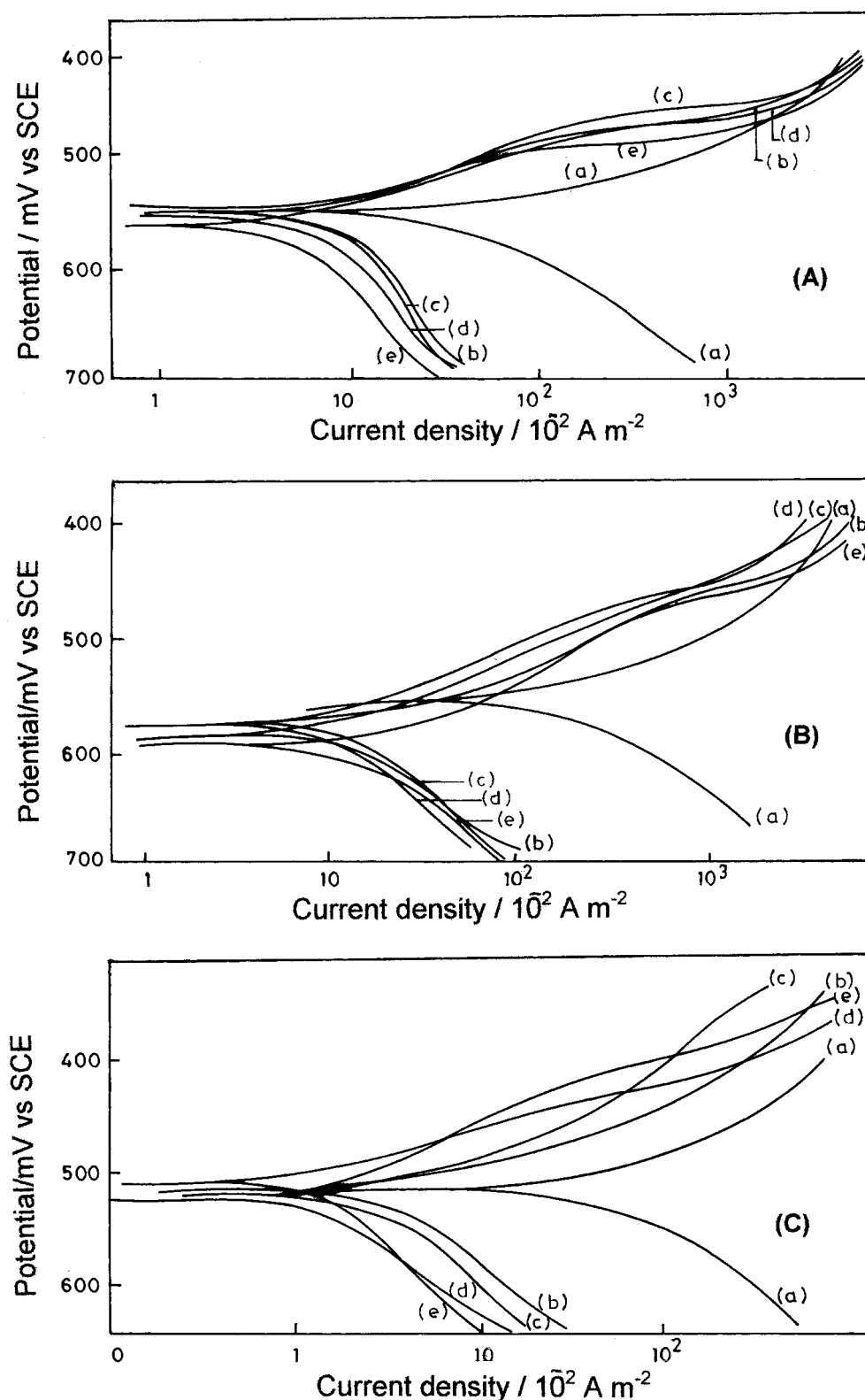


Fig. 3. Potentiodynamic polarization curves for mild steel in (A) 1 M HCl, (B) 3 M HCl and (C) 5 M HCl containing 500, 700 and 1000 ppm of dithiobiurets. Curves (a) blank, (b) CPDTB, (c) DPDTB, (d) TPDTB and (e) APDTB.

of APDTB are shown in Figure 6(a, b). The appearance of peaks at 152 and 378 eV, respectively indicates the adsorption of APDTB on the metal surface through S and N atoms.

4. Conclusion

The main conclusions are as follows:

- (i) All the substituted dithiobiurets show good inhibition efficiency in the range 1–5 M HCl.

Table 3. Inhibition efficiencies obtained for different concentrations of dithiobiurets derivatives from weight loss measurements in absence and presence of KI

System	Inhibitor concentration /ppm	R_t / Ω cm ²	C_{dl} / μ F cm ⁻²	I_{corr} /A m ⁻²	IE /%
1 M HCl	—	115	12832	155	—
APDTB	300	1500	937	10.05	94.03
	500	2140	845	8.71	94.63
TPDTB	300	1400	1029	12.14	93.83
	500	2000	866	9.86	94.25
DPDTB	300	750	1832	24.35	86.44
	500	900	1729	22.31	87.24
CPDTB	300	650	2350	26.83	83.94
	500	800	1947	25.43	85.63

- (ii) The IE of all compounds increases with increase in inhibitor concentration, temperature and immersion time, whereas it decreases with increase in acid concentration.
- (iii) The IE of the substituted dithiobiurets follows in the order: APDTB > TPDTB > DPDTB > CPDTB.
- (iv) The adsorption of all the compounds on mild steel from acidic solution obeys a Temkin adsorption isotherm.
- (v) The potentiodynamic polarization study shows that APDTB and DPDTB behave as mixed inhibitors whereas TPDTB and CPDTB act predominantly as cathodic inhibitors.

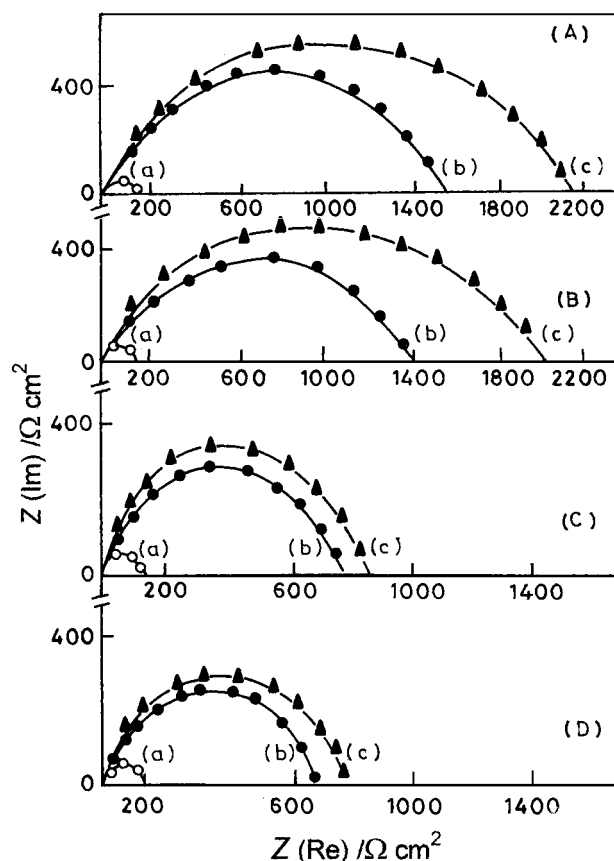


Fig. 4. Nyquist plots for mild steel in 1 M HCl in absence and presence of different concentrations of dithiobiurets: (a) blank, (b) 300 ppm and (c) 500 ppm. For: (A) APDTB, (B) TPDTB, (C) DPDTB and (D) CPDTB.

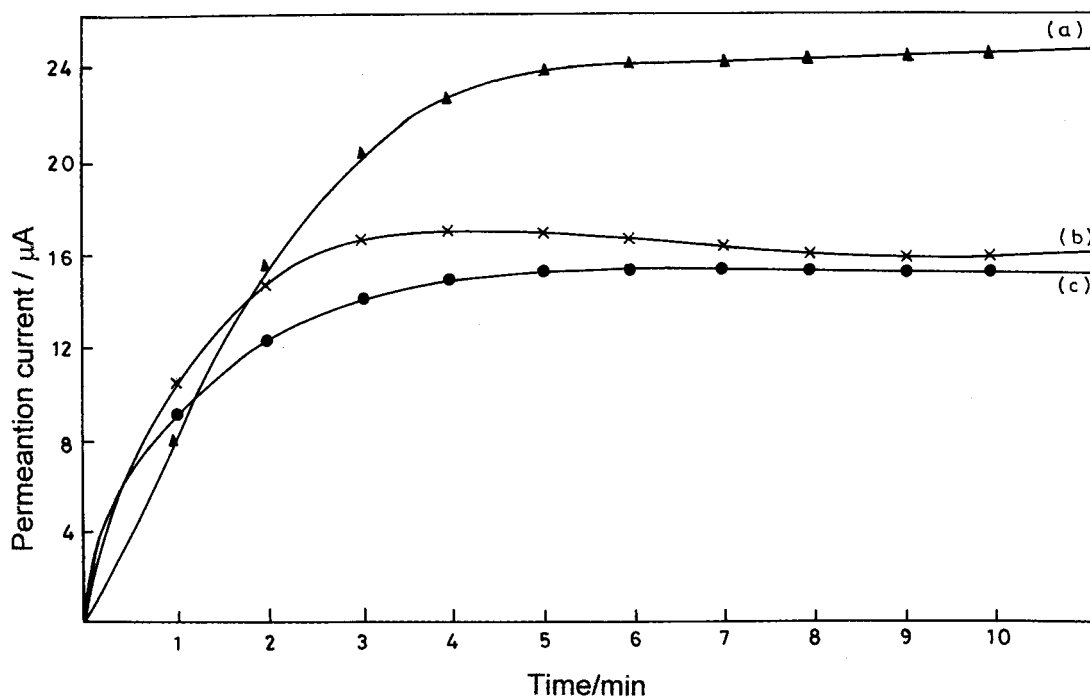


Fig. 5. Curves of hydrogen permeation current against time for mild steel in 1 M HCl in absence and presence of 500 ppm of dithiobiurets. For: (a) blank, (b) CPDTB and (c) DPDTB.

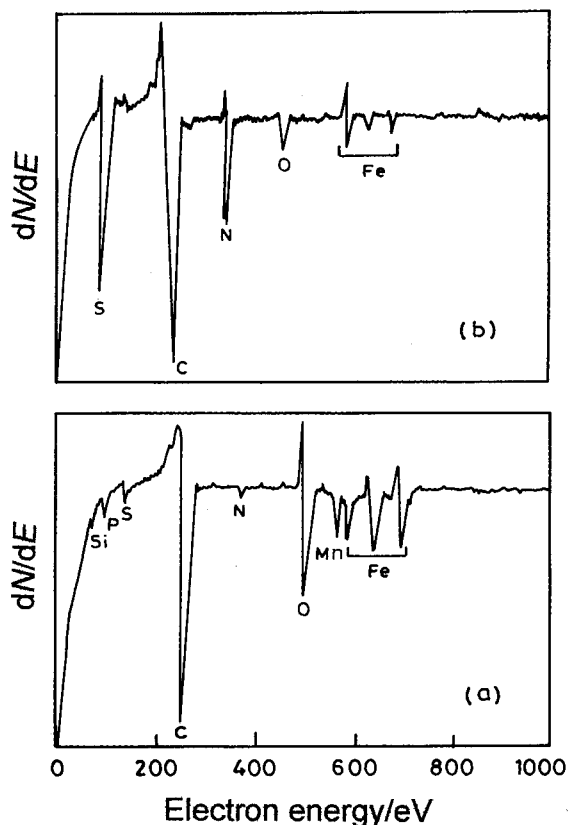


Fig. 6. AES spectrum for (a) polished mild steel surface (b) mild steel exposed to APDTB.

- (vi) Electrochemical impedance spectroscopy shows that R_t values increase, while C_{dl} and I_{corr} values decrease in the presence of dithiobiurets.
- (vii) Both the tested compounds namely CPDTB and DPDTB, reduce the hydrogen permeation current.
- (viii) AES analysis confirms the adsorption of APDTB on mild steel through nitrogen and sulphur atoms.

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